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Mixed Ligand Complexes of Zinc Benzoylacetonate with Substituted Pyridines and Quinolines

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Received December 15, 1969

Zinc benzoylacetonate was reacted in ethanolic medium with several substituted pyridines and quinolines and eleven, non-electrolytic, pentacoordinated mixed ligand complexes having the general composition $[Zn(bzac)_2L]$ have been isolated and characterised. The infra-red spectra indicate the presence of both benzoylacetone and the bonded ligand.

Introduction

Divalent zinc ion has a completely filled $3d^{10}$ nonbonding shell and hence uually forms four-coordinated tetrahedral complexes utilising $4s4p^3$ hybrid orbitals for bonding. Under favourable conditions, the coordination number can increase to 5 to 6 involving $4s4p^34d$ or $4s4p^34d^2$ orbitals. We have been trying the complex formation using mixed ligands with different electro-negativities of the donor atoms and reported several complexes of cobalt(II),[1] cadmium(II),[2] nickl(II)[3] and zinc(II)[4,5] containing hetero ligand atoms. In this communication we report some pentacoordinated mixed ligand complexes of zinc(II) containing bonded benzoylacetone and substituted pyridine or quinoline.

Experimental Section

All the materials used were of A.R. grade. The starting material zinc benzoylacetonate was prepared according to a known method by treating an ethanolic solution of zinc chloride with benzoylacetone (ethanolic solution) in stoichiometric ratio followed by dropwise addition of ammonia. The mixture was vigorously shaken. The precipitated compound was filtered, washed with ethanol and ether and dried *in vacuo*. Analysis of the compound corresponds to the cmposition $[Zn(bzac)_2 . H_2O]$. The I.R. spectrum of this compound has now been recorded which shows an absorption band at 3400 cm^{-1} (s) attributable to coordinated water in addition to the characteristic bands of bonded benzoylacetone.

Preparation of the mixed ligand complexes. A suspension of zinc benzoylacetonate in ethanol was refluxed with different ligands containing nitrogen donor atoms in 1:2 ratio for two to three hours. The clear solution obtained was kept standing overnight or in some cases for two days when crystalline compounds separated out. They were washed with ethanol followed by ether and dried *in vacuo*.

The purity of the isolated compounds was established by estimating the metal as zinc ammonium phosphate. Even though the percentage of metal in these complexes is quite diagnostic, carbon and hydrogen were estimatd in the case of two compounds $[Zn(bzac)_2(3-Etpy)$: Found: C, 64.98; H, 5.15; Reqd. C, 65.46; H, 5.49; $Zn(bzac)_2$ (Q): Found: C, 67.14; H, 5.15; Reqd. C, 67.53 H, 4.83] and the results are in conformity with the composition determined by estimation of metal. The conductance measurements were carried out in $M/1000$ acetone solution using a Toshniwal conductivity bridge. The presence of mixed ligands in the complex was established by infra-red spectra recorded on a Unicam SP200 spectrophotometer. The melting point, analyses and conductance data of the complexes are given in Table I.

Results and Discussion

Mehta and Dessai reported[6] the determination of diamagnetic susceptibility of bis-(benzoylacetonato)-zinc(II), but the methed of preparation was not described in detail. Graddon and Weeden prepared[7] this compound by reaction between zinc hydroxide and benzoylacetone as methanol bis-(benzoylacetonato)zinc(II) after crystallisation from methanol. They also obtained the anhydrous compound and a series of adducts with heterocyclic bases and ammonia. From molecular weight determination, Graddon *et. al.* showed $[Zn(bzac)_2]$ to be monomeric in solutions in non-donor solvents and presumably tetrahedral. They could not find any evidence for polymerisation in contrast to the corresponding nickel(II) compound which had been shown to attain octahedral configuration by trimerisation.[8]

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Table I. Analyses, melting point and conductance data of zinc benzoylacetonato complexes with nitrogen donor ligands

Compound	Colour	form	M.P. (°C)	Conductance (mhos)	% Zinc Found	% Zinc Reqd.
[Zn(bzac)$_2$. IQ]	White	needles	115	0.21	12.71	12.65
[Zn(bzac)$_2$. Q]	White	crystals	230	0.21	12.59	12.65
[Zn(bzac)$_2$. (2—Am—Py)]	White	crystals	135	0.23	14.06	13.57
[Zn(bzac)$_2$(3—Am—Py)]	White	needles	144	0.22	13.62	13.57
[Zn(bzac)$_2$(4—Am . Py)]	White	needles	205	0.21	13.74	13.57
[Zn(bzac)$_2$(2—Am . 4—MePy)]	White	crystal	142	0.20	12.86	13.16
[Zn(bzac)$_2$(3,5—Lut)]	White	plates	128	0.18	13.35	13.21
[Zn(bzac)$_2$(β—Pico)]	White	needles	107	0.19	13.24	13.59
[Zn(bzac)$_2$(4—Et . Py)]	White	needles	109	0.31	13.09	13.21
[Zn(bzac)$_2$(3—Et . Py)]	White	needles	106	0.34	12.97	13.21
[Zn(bzac)$_2$(4—Vpy)]	White	needles	92	0.18	13.04	13.26

Table II. Infra-red spectra of Mixed Ligand Complexes of Zinc(II) (cm^{-1})

Compound	ν(C—C)	ν(C—O)	ν(C—O) δ(C—H)	Bands due to bonded ligand L*
Benzoylacetone	1613 vs	1581 sh	1555 sh	
[Zn(bzac)$_2$. H$_2$O]	1603 s	1568 w	1518 m	
[Zn(bzac)$_2$. L]				
where L is				
Isoquinoline	1591 vs	1568 w	1503 w	745 s, 810 m, 928 s, 1620 w (755 s, 840 s, 960 s, 1622 vs)
Quinoline	1603 s	—	1521 vs	742 s, 788 vs, 1410 m, 1630 w (756 s, 805 vs, 1448 s, 1635 s)
2—Am . Pyridine	1593 s	1553 s	1515 s	852 s, 1280 s, 1603 w, 3350 m (880 s, 1290 s, 1615 s, 3400 s)
3—Am . Pyridine	1600 s	1565 w	—	697 s, 1350 w, 1405 m, 1640 w, 3350 m, (710 s, 1395 m, 1445 m, 1640 m, 3450 s)
4—Am . Pyridine	1600 s	1573 br	1530 br	700 vs, 822 vs, 1485 w, 1613 s, 3300 s (700 s, 845 s, 1510 sh, 1650 vs, 3400 s)
2—Am, 4—Me . Pyridine	1593 vs	1563 w	1535 br	700 vs, 865 s, 1282 m, 1643 m, 3400 br (740 s, 880 vs, 1320 vs, 1643 s, 3400 s)
β—picoline	1598 vs	1568 s	1520 s	742 s, 945 s, 1410 s, 1487 w (770 s, 990 s, 1415 vs, 1495 m)
3—ethyl pyridine	1605 vs	1583 s	—	798 s, 938 s, 1125 vs, 1435 vs (810 s, 970 s, 1175 s, 1455 s)
4—ethyl pyridine	1598 s	1565 s	1515 br	740 s, 1020 s, 1207 s, 1410 m (770 s, 1055 m, 1213 s, 1415 m)
4—vinyl pyridine	1605 s	1575 m	1510 br	795 s, 842 s, 938 s, 1270 s, 1413 w, 1510 br (808 vs, 852 vs, 950 s, 1295 m, 1422 vs, 1558 vs)
3,5—lutidine	1592 vs	1563 m	1535 br	695 s, 845 s, 1415 s, 1285 br (702 vs, 860 vs, 1420 vs, 1315 s)

* The corresponding free ligand absorption is indicated in parenthesis; s, sharp; vs, very sharp; m, medium; br, broad, w, weak; sh, shoulder.

Belford and coworkers determined[9] the crystal and molecular structure of ethanol bis(benzoylacetonato)-zinc(II) and showed that the coordination aruond the metal ion is close to square pyramidal with slight departure due to twisting of one of the chelate rings. In this respect the structure of [Zn(bzac)$_2$. C$_2$H$_5$OH] differs from that of [Zn(acac)$_2$. H$_2$O] in which there is a significant distrotion towards a trigonal bipyramidal configuration.

The compounds reported in this investigation have a general formula [Zn(bzac)$_2$L] where L is the hetero ligand. The infra-red spectra show the characteristic bands of the ligands and further the band due to coordinated water at 3400 cm^{-1} completely disappears. There is considerable overlapping of the bands due to benzoylacetone and the bonded nitrogen donor ligands. Only those bands which are definitely attributable to the nitrogen ligands in addition to ν(C—C) and ν(C—O) of benzoylacetone[10] were given in Table II.

The absorption bands of the free ligand are indicated in parenthesis. It can be seen that most of the ligand absorption bands are shifted to a lower frequency due to bonding of the ligands to the metal replacing the water molecule. Further definite changes are also observed in the C—O and C—C stretching frequencies by the introduction of hetero ligand (L). It is thus clear that both benzoylacetone and hetero ligands are bonded to the metal. The metal analysis can distinguish beyond doubt the presence of one or two moles of the ligand since they have large molecular weights and impose large differences for different compositions. All the compounds reported in this communication do not contain any coordinated water, answer to the formula [Zn(bzac)$_2$L], have low melting points and are non-electrolytes. Hence

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they are all penta-coordinated. In addition to the penta-coordinated base adducts of zinc acetylacetonate reported[11] by Graddon *et. al.*, the terperidyl zinc chloride[12] and aquo disalicylidene (ethlene diaminato)-zinc(II)[13] were also shown to exhibit a coordination number of five. Recently we reported[5] some penta-coordinated heterocyclic base adducts of zinc acetylacetontae. The compounds reported in this communication are a few more examples for penta-coordination in zinc complexes. X-ray investigations on these compounds will be helpful to indicate the exact preferred stereochemistry either trigonal bipyramidal or square pyramidal.

Acknowledgments. Thanks are due to the Ministry of Education, Government of India for the award of a Research Training Scholarship to one of us (B.K.M.).

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